

THE FRANKLIN INSTITUTE • Laboratories for Research and Development

Quarterly Progress
Report No. P-2236-11

PERMANENT MAGNET MATERIALS

July 1, 1953 to September 30, 1953

Prepared for
Chief of Naval Research, Department of the Navy
Under Contract No. Nonr-01002

Approved by:

Foster Nix

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Associate Director

Approved by:

Nicol H. Smith

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Director

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ABSTRACT

The study of the CaH_2 reduction process for the preparation of single-domain powders is almost complete. While a detailed discussion of the results of this study will not be made until the next quarterly progress report, the major conclusion can be stated. The lower limit to the particle size of the final product is determined by the temperature at which the initial starting material, ferrous formate, is decomposed thermally to the intermediate compound, FeO . The temperature of reduction of the FeO to Fe is important for the Fe particle size only in that sintering can cause particle growth above the lower limit.

Some preliminary data on pressed bars of single domain powders are briefly discussed.

The results of a study of the broadening of X-ray diffraction lines in "as prepared" and annealed carbonyl Fe are given in detail. The mean crystallite diameter is of the order of 50-80 Å and strains are present in the lattice whose magnitude is of the order of 2×10^{-3} to 6×10^{-3} in the "as prepared" material. After two hours of annealing the strains are relieved below about 350°C ; crystal growth does not start until this temperature is reached.

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1. INTRODUCTION

1.1 Purpose

More and more, relationships that exist between the structures of ferromagnetic materials and their magnetic behavior are coming to light. It is the purpose of this program to study these relationships in the case of permanent magnet materials. In particular, the relationship between coercive force and particle size in fine powders will be given special emphasis.

1.2 Scope

To investigate the fundamental properties of permanent magnet materials.

2. PRESENT STATUS AND PROGRESS

2.1 Introduction

The work of the past quarter to be reported here will be divided into three sections. These are:

- (a) The reduction process for the production of Fe powders;
- (b) Magnetic properties of powder compacts; and
- (c) X-ray line broadening by carbonyl Fe.

2.2 Reduction Process for Preparation of Fe Powders

Quarterly Progress Report No. P-2236-10 describes the development and details of a reduction process in which CaH_2 is used to reduce FeO to produce single-domain Fe powders. The FeO is obtained by the thermal decomposition of ferrous formate. The work reported at that time suggested that the lower limiting size of the Fe powder produced from any one batch of FeO was controlled by the temperature at which the decomposition of ferrous formate took place. During the past quarter, the influence of this decomposition temperature has been

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further studied, and the results have quite definitely confirmed the suggestion. In the table below, Fe particle sizes are listed for three different FeO samples, all reduced to Fe at identical temperatures.

	<u>Particle Size for Reduction at</u>	
<u>T₁</u>	<u>200-210°C</u>	<u>300°C</u>
255°C	250 Å	385 Å
235	190	300
220		265

In the first column, under the heading T_1 , are listed the temperatures at which thermal decomposition of ferrous formate to FeO took place. The second column lists the particle sizes of the resulting Fe powder for reduction of the FeO at temperatures in the neighborhood of 200-210°C, and the third column gives the particle sizes for reduction at 300°C. In each case, the particle size decreases with decreasing thermal decomposition temperature.

The range of sizes produced by this process now covers the single-domain particle size range. Coercive forces for zero magnetization as high as 700 Oe in pressed bars of the Fe powder have been obtained. The study of this reduction process is almost completed, and the details of the findings will be reported in the next quarterly report.

2.3 Magnetic Properties of Pressed Bars of Single-Domain Fe Powders

Two series of samples have been prepared, each from a single-domain Fe powder produced during the course of the study of the reduction process.

In the first series, samples were pressed at pressures of 12, 20, 60 and 100 tsi. Samples with the last three pressures were pressed by Mr. Edward Stewart, of the Metallurgy Department of Lehigh

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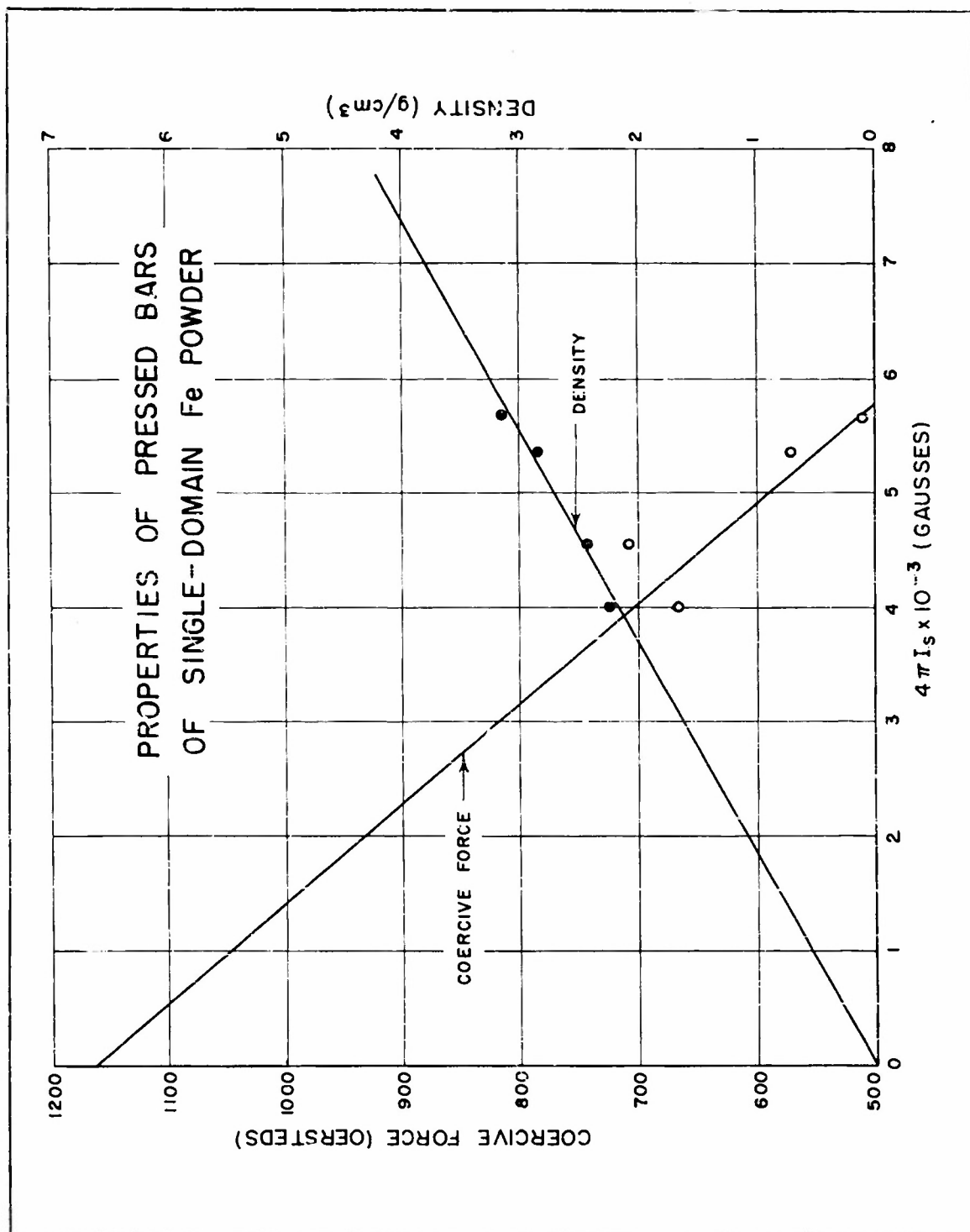
University. The bar pressed at 12tsi was prepared here. The initial powder was found to contain 80 percent free metal by hydrogen evolution.

Values for the saturation magnetization for each sample were obtained by plotting magnetization values as a function of the inverse field strength, and extrapolating to infinite field strength. In Figure 2.1, these saturation magnetization values are plotted as abscissae, and the sample densities and coercive forces are plotted as ordinates. An approximate straight-line relationship exists between the saturation magnetization and the density, indicating that the saturation magnetization is a reasonable measure of the volume fraction of the sample occupied by the powder. The coercive force values show considerable scatter. A rough extrapolation to infinite dilution, represented by zero on the saturation magnetization axis, gives an ultimate coercive force in the neighborhood of 1000 to 1100 Oe. This value indicates that the particles are definitely single domain.

The saturation moment per gram for the sample was of the order of 1840 gauss per gram, expressed as $4\pi I_s/\text{density}$. This value is definitely low compared to the expected value of 2730 for pure Fe. It is low even when the pure Fe value has been corrected for the 80 percent free metal in the initial powder. However chemical analysis of the 100 tsi sample, by hydrogen evolution, indicated a free metal concentration of 60 percent. Apparently some oxidation of the powder occurred before or during pressing.

BH_{max} values for all four of the samples were of the order of $4 \times 10^5 \text{ ergs/cm}^3$. This low value is undoubtedly related to the low saturation per gram of the samples. This type of study will be continued with other single domain powders that are now being produced.

A second set of pressed samples has been prepared from a similar single domain powder. The powder, analyzed by hydrogen evolution, contained 60 percent free metal. These samples were all pressed at



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FIGURE NO. 2-1

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12tsi, but contained varying amounts of SiO_2 powder to provide magnetic dilution. Complete hysteresis loops and normal induction curves have been obtained for these samples. The object of this work is to analyze these hysteresis loops in terms of domain theory, so that predictions may be made about the effects of varying concentration, mixtures of powders of different coercive forces, etc., upon the magnetic properties of powder compacts. The analyses are now in progress and will be reported upon in detail when they are finished. One point of interest has already been noticed, in that the coercive force is not proportional to the volume fraction of the sample occupied by the ferromagnetic phase, in contrast to the results of Weil¹ for single domain powders. This may be due to the method used in dispersing these powders with the SiO_2 .

2.4 X-ray Line Broadening by Carbonyl Fe

2.4.1 Introduction

In Quarterly Progress Report P-2236-6, dated June 30, 1952, work on the measurement of particle size using three different techniques was reported. One of the techniques studied was the broadening of X-ray diffraction lines. In the course of this study, it was noted that the crystallite size in "as prepared" carbonyl Fe, as determined by the broadening of the X-ray diffraction lines, was very much smaller than the particle size given by the electron microscope. For example, as shown in Table 2.1 of that report, for the carbonyl Fe labelled P-818 the electron microscope particle size was of the order of 1.7 microns, whereas the crystallite size from the X-ray studies was about 130 Å. This effect is well recognized in the carbonyl Fe industry, and is attributed simply to a polycrystalline structure of the metal particles. A further feature of this material is the fact that this apparent difference between particle size and crystallite size disappears readily for rather low annealing temperatures, of the order of 400°C. This is a rather surprisingly low temperature for grain growth in Fe.

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As a by-product of the study of the methods for determining particle size, a fairly detailed investigation of the X-ray line broadening in this carbonyl Fe was made. The contribution to the line broadening caused by both strain and crystallite size was determined, and some observations upon the annealing process were made. The results of this study will be reported in detail here. The first part will contain a detailed analysis of the situation in the carbonyl Fe as it is first prepared, before any annealing treatment. In the second part will be presented the results of the study of the annealing process.

The material used throughout this study was the experimental carbonyl Fe designated P-818, and supplied through the generosity of General Aniline and Film Corporation. The composition of the material according to chemical analysis was as follows:

Iron	- 97.89 Wt. %
Carbon	- 0.71
Hydrogen	- .54
Remainder, presumably	- .86
Oxygen	

The particles, as observed with both the optical and electron microscope, were quite spherical and possessed an average diameter of about 1.7 microns, as mentioned above.

2.4.2 Strain and Crystallite Size in the Untreated Powder

The Experimental Method - The line profiles needed for the analyses were obtained from powder briquettes 1/8" x 1/4" x 1", pressed at 12 tsi from the "as prepared" powder with a binder of duco cement. The intensities were determined by a point-by-point count using a conventional Geiger counter spectrometer. An average of 75 points were taken each time the line was "counted", and each line was "counted" three times. Line profiles of each diffraction line were taken for

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both the sample exhibiting line broadening and for a well annealed sample, or "standard". The diffraction peaks were corrected for instrumental broadening, including the $K\alpha$ doublet, by the method given by Stokes², using the Lipson-Beevers³ strips. The corrected line profiles, whose breadth was due only to crystallite size and distortion, were expressed in terms of the coefficients A_L of Fourier series.

A total of nine lines were studied using Mo $K\alpha$ radiation: the (110), (211), (220), (321) and (422); the (200) and (400); and the (222) and (444). The (110), (211), (220) and (200) lines were also analyzed using Fe $K\alpha$ radiation. These lines gave information about three directions in the crystal, namely those perpendicular to the (110), (100) and (111) planes. The fact that (110), (211) and (321) planes gave identical values is an interesting result of the experiment.

Inasmuch as iron is elastically anisotropic and the coefficients A_L contain an explicit contribution produced by strain in the lattice, it is interesting that those lines which correspond to directions in the crystal having the same value of Young's modulus yielded identical results. The set of lines including the (110), (211), (220), (321) and (422) all represent directions in the iron crystal which have a Young's modulus of 22,500 Kg/mm². These planes are the slip planes in iron. In the cases of the (100) and the (111) sets of lines, no other directions were found which had similar Young's moduli. These planes correspond to directions in the crystal having the minimum value (fracture planes) and the maximum value of Young's modulus, respectively. A similar correlation with the values of Young's modulus was observed by McKeehan and Warren⁴ for the case of cold-worked, thoriated tungsten.

The technique used to separate the strain broadening from the broadening caused by crystallite size was that described by Warren and Averbach (5,6,7,8). They have shown that for either type of broadening the shape of the diffraction peak can be represented by a

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Fourier series:

$$P = K \sum_{n=-\infty}^{+\infty} A_L(l_0) \cos \left(\frac{4\pi}{a} L \sin \theta \right) \quad (2.1)$$

where

$$l_0 = \sqrt{h^2 + k^2 + l^2};$$

h, k, l are the Miller indices; and $L = na_3$,
where n is the defining integer of the Fourier
coefficients and a_3 is a length in the crystal.

Further, they have shown that if both types of broadening are
present, the coefficients $A_L(l_0)$ may be written as a product of
coefficients, each representing one type of broadening:

$$A_L(l_0) = A_L^P \cdot A_L^D(l_0) \quad (2.2)$$

where, for crystallite size:

$$A_L^P = \frac{1}{N} \sum_{i=|n|+1}^{\infty} (1 - |n|) n_i \quad (2.3)$$

and for distortion,

$$A_L^D(l_0) = \left\langle \cos \frac{2\pi l_0 \Delta L}{a} \right\rangle_{av.} \quad (2.4)$$

Here, n_i is the number of columns of unit cells, of length i cells,
perpendicular to the reflecting planes; N is the total number of cells;
 a is the lattice parameter; and ΔL is the change in L for a given value
of L .

The coefficient A_L^P is independent of the order of the diffraction line, while A_L^D can be approximated, for small n and l_0 , by an exponential the argument of which is proportional to the square of the order, as well as to the mean square strain.

$$\left\langle \cos \frac{2\pi l_0 \Delta L}{a} \right\rangle_{\text{ave}} \approx \exp \left[- \frac{2\pi^2 l_0^2 \langle (\Delta L)^2 \rangle}{a^2} \right]$$

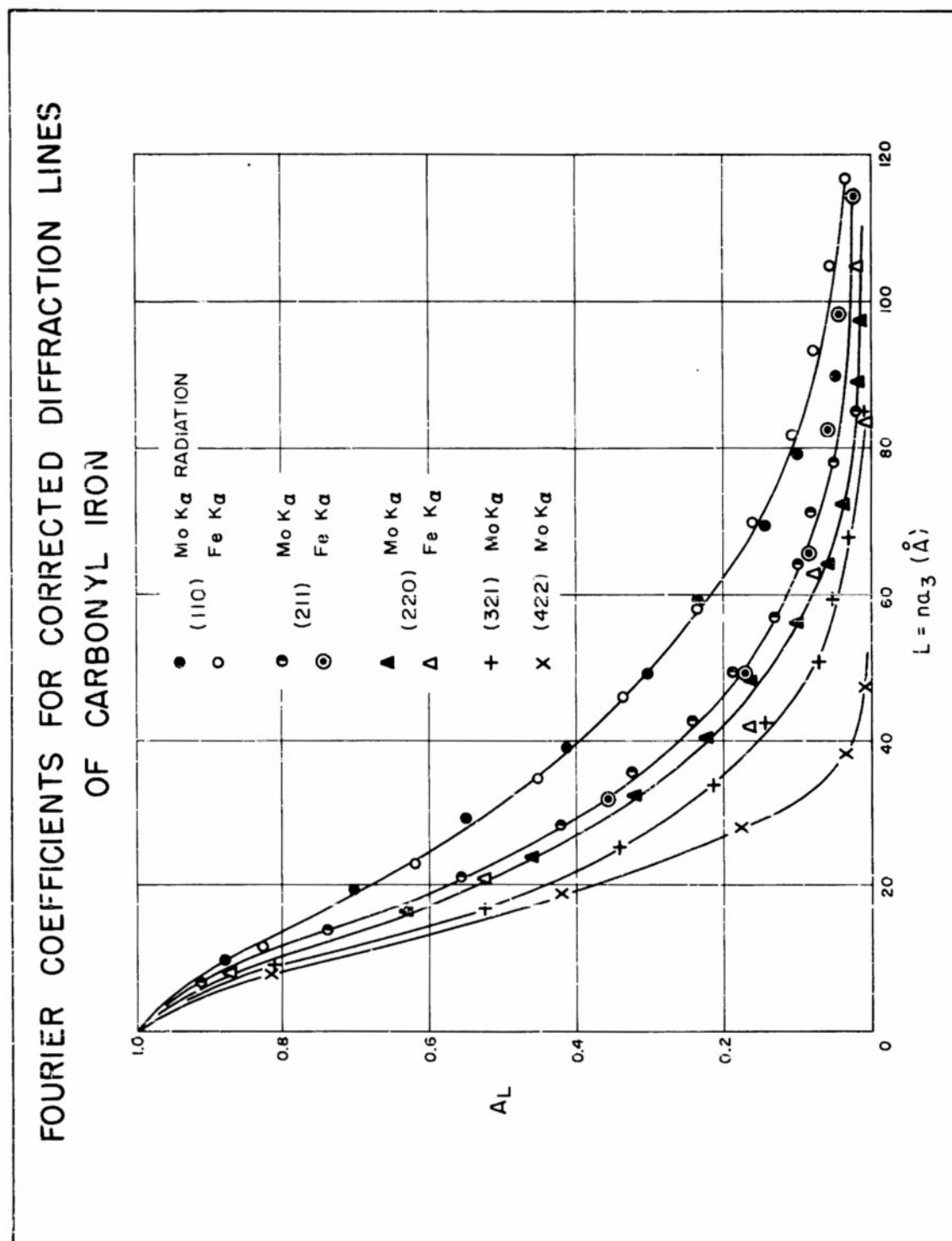
Thus, if we plot the logarithm of A_L vs. the square of the order of the lines for fixed L , the intercepts on the axis of ordinates give $\ln A_L^P$, and the initial slopes are proportional to the mean square strains,

$$\left\langle \left(\frac{\Delta L}{L} \right)^2 \right\rangle = \langle \epsilon^2 \rangle .$$

The coefficients, A_L , of the line profile obtained by correcting the broadened lines for instrumental broadening, were plotted against the parameter L . Figure 2.2 shows the resulting curves for the five lines of the (110) set.

Values of A_L for constant values of L were taken from this set of curves and the logarithm of A_L plotted as a function of the square of the order of the diffraction lines, as shown in Figure 2.3. The intercepts of these curves on the axis of ordinates gave the logarithm of the crystallite size coefficients, A_L^P , and the initial slopes gave the mean square strains.

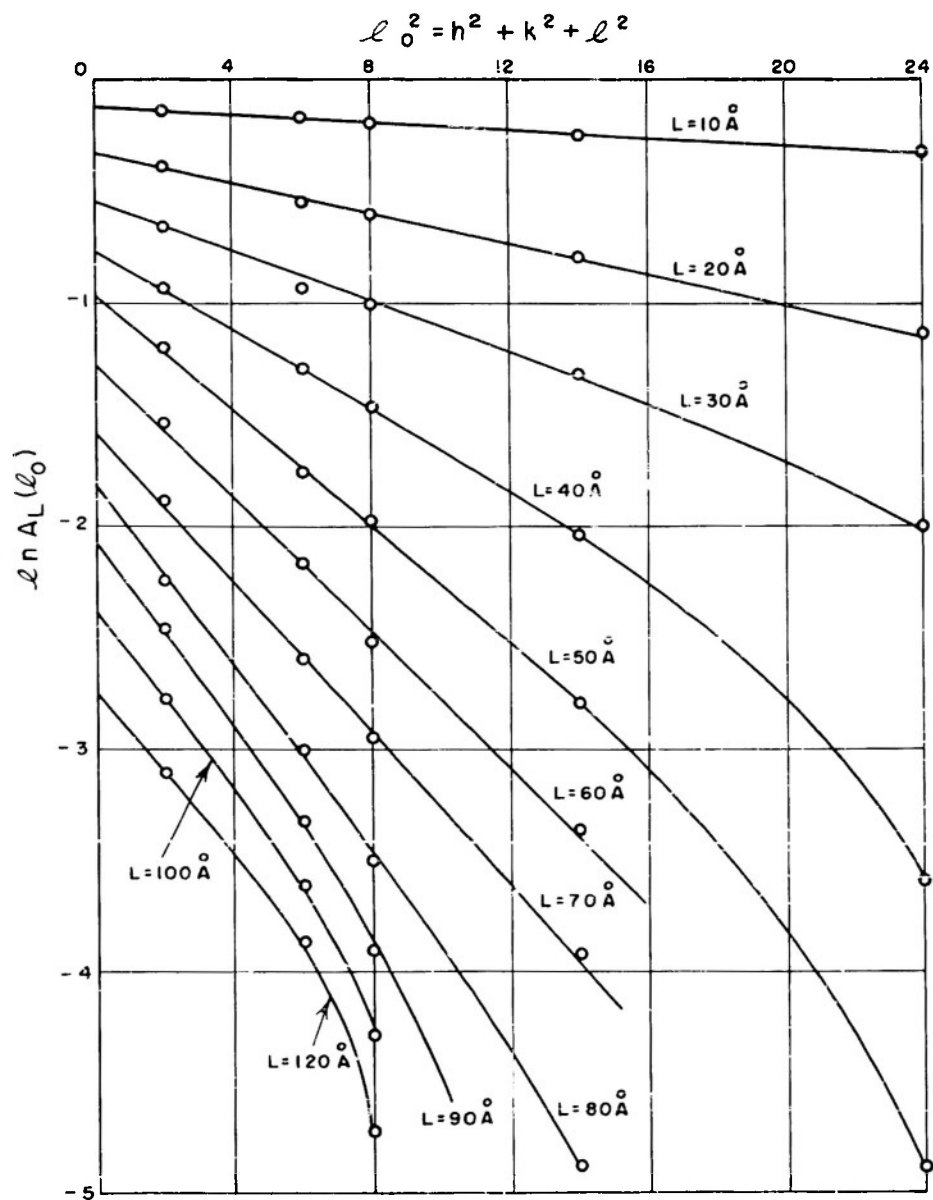
Results - Figure 2.4 gives the curve of the crystallite size coefficients as a function of the length of a column of cells in the crystal. The mean size of the crystallites is then given by the reciprocal of the negative initial slope of this curve. The value obtained in the $[110]$ direction (from Fig. 2.4) is approximately 70 Å.



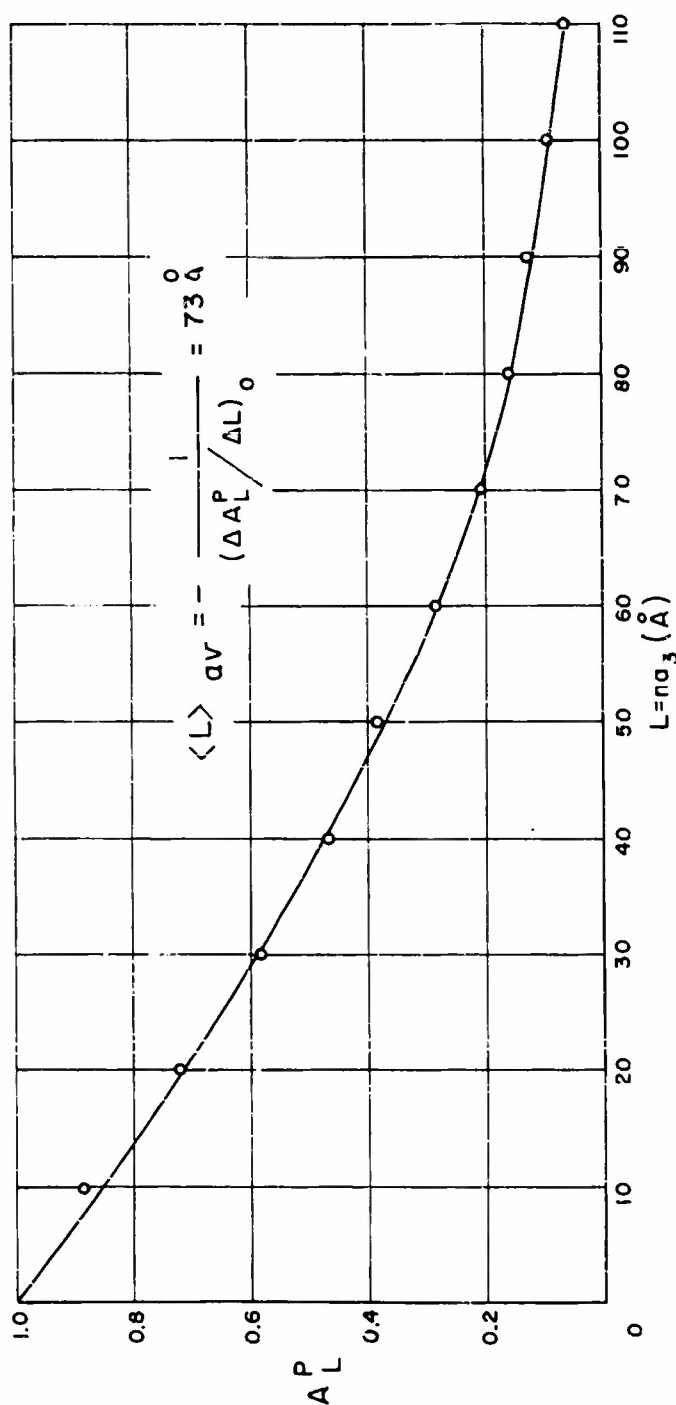
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FIGURE NO. 2-2

VARIATION OF FOURIER COEFFICIENT LOGARITHMS WITH DIFFRACTION LINE ORDER FOR CARBONYL IRON



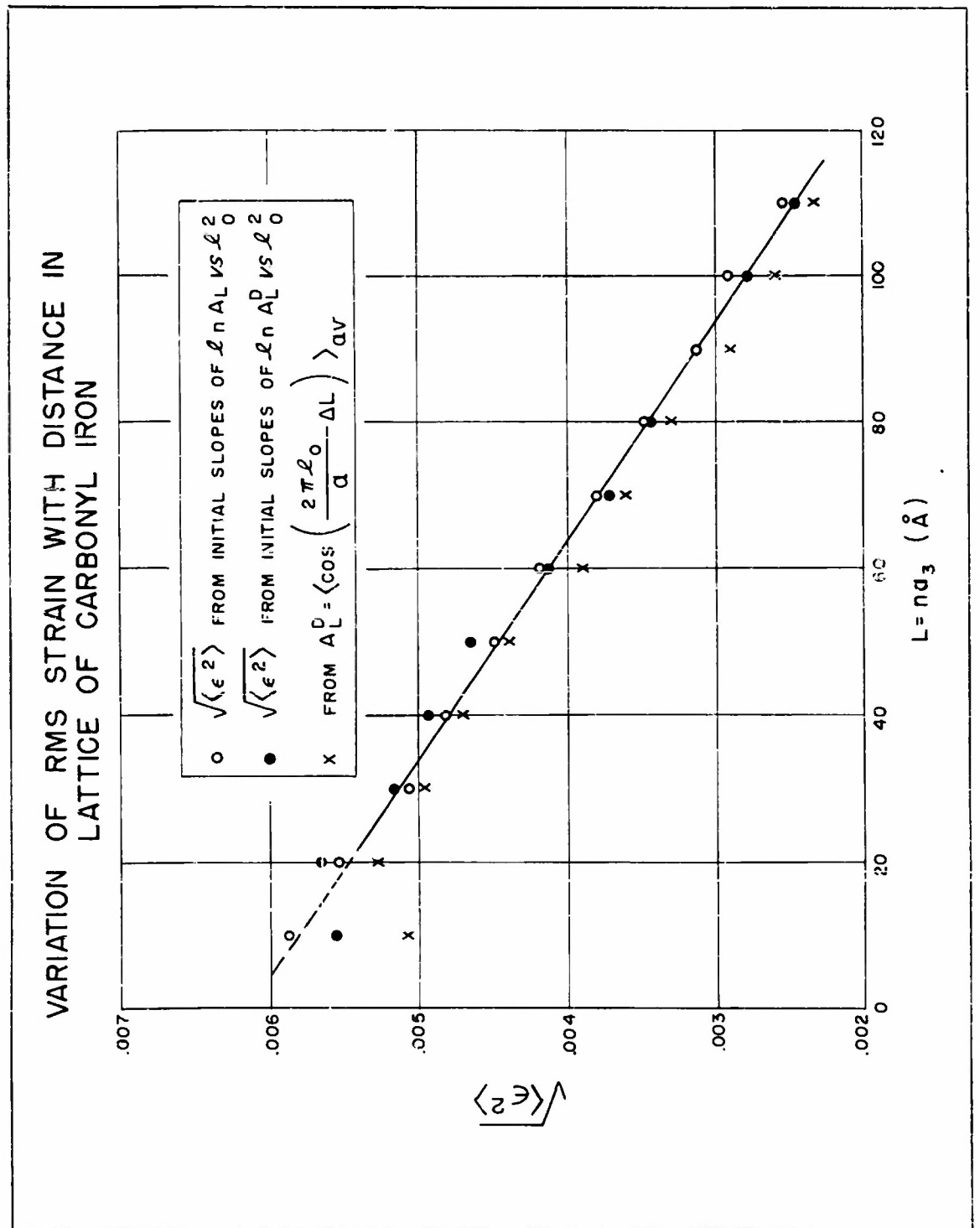
VARIATION OF PARTICLE-SIZE DEPENDENT PART OF
FOURIER COEFFICIENT OF (110) DIFFRACTION LINE WITH
DISTANCE IN LATTICE IN CARBONYL IRON



The term "mean crystallite size" or "dimension" as used here indicates the measured value of the mean length of a column of cells in the crystallite, the columnar axes of which are along the given direction. Consequently the reported values are not true dimensions of a crystallite, since it is possible to show that the mean length of columns of cells, \bar{L} , is always less than the largest crystallite dimension.

Figure 2.5 gives the mean square strain as a function of distance in the crystal. These strains can be computed in three ways, as indicated in the figure. As mentioned above, they can be computed from the initial slopes of the curves of $\ln A_L$ vs l_o^2 . In addition, one can obtain values for the A_L^P from the plot of A_L^P vs L , which then can be divided into A_L to give the coefficients, A_L^D , caused by distortion broadening. From these, one can compute strain from the cosine representation (Eq. 2.4), or, assuming the exponential approximation to be valid, we can compute the rms strains from a plot of the logarithm of A_L^D vs l_o^2 . In view of the relatively large error inherent in taking slopes of logarithmic curves, the agreement is good.

Using analyses entirely similar to the one described for the (110) set of lines, we have obtained the values of the crystallite size and strain for the $[100]$ and $[111]$ directions in this material. Table 2.1 gives the maximum values of the strains and the mean crystallite sizes in these directions, along with those for the $[110]$ direction.



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Table 2.1 Crystallite Size and Strain in Untreated Carbonyl Fe Powder

Crystal Direction	Mean Crystallite Size (Å)	rms Strain	Young's Modulus	Stress* (Kg/mm ²)
[100]	53	3.5×10^{-3}	13,500	37
[110]	73	6.3×10^{-3}	22,500	142
[111]	80	2.2×10^{-3}	20,000	64

* Computed using a Hooke's law relation.

We have included in the table the values of Young's modulus for the given directions, and the values of the stresses corresponding to the strains if a Hooke's law is assumed to hold.

Discussion of Results - The data indicate that there is an rms strain of about 6×10^{-3} in the [110] direction over very small distances. It was observed from lattice parameter measurements (see Section 2.4.3) that there was an average macroscopic strain of about 2.7×10^{-3} in this direction. Thus, the evidence is that there is a combination of micro- and macro-strains, where by micro-strains are meant those strains with equal probability of being positive or negative, and whose regions of influence extend only over small distances in the crystal. It is to be noted that the method of analysis used will give rms strains which tend to go to zero at distances comparable with the dimension of the largest crystallite even if no micro-strains be present.

Very little significance is to be attached to the stresses given in Table 2.1, since the validity of Hooke's law is extremely uncertain. Strain here may be either plastic or elastic, or both. However, there is a definite correlation with the elastic anisotropy of the material as is shown by the fact that all lines of the set, referred to as the (110) set, give similar values.

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The values of the stresses given in Table 2-1 can be compared with Taylor's values⁹ for the stress in carbonyl Fe which were computed in a similar manner. Using a different carbonyl iron powder (Mond Nickel Co.) and a different technique for determining the strain, Taylor obtained a value for the stress of about 130 tsi. This compares favorably with the present value of approximately 100 tsi. However, Taylor found a crystallite size of 200 Å, which is considerably larger than the present values. Bertaut,¹⁰ on the other hand, found the broadening of the line from carbonyl Fe powder to be due entirely to crystallite size of about 70 Å. In a private communication he stated that his work indicated negligible strain. However, his conclusions were based on the analysis of a single (110) line, which does not allow precise determination of the strain. Thus, the fact that his values agree with our results is probably due to two opposing factors: (1) his crystallites were larger than ours, and (2) his analysis neglected the effects of strain, which would reduce the apparent crystallite size.

The results in Table 2.1 for the $[100]$ and $[111]$ directions were obtained using only two diffraction lines per set, of which one in each set was a relatively weak line and consequently difficult to analyze. Thus, for these cases the values must be considered as approximate. However, the results are sufficiently clear to indicate that this Fe carbonyl powder exhibits anisotropy in both strain and crystallite size.

It would seem reasonable to suppose that a material deposited from the vapor phase should be free of strain. However in this case the deposition process is such as to produce results very similar to a quenching process and in addition the product is not a pure substance. The untreated carbonyl Fe is only 98 percent Fe and the impurity atoms (carbon, nitrogen and oxygen) probably play a major role in producing the strain. If the lattice is to accommodate these impurity atoms, it must strain itself in doing so and this is possibly the major cause of the measured strain.

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If the strain is sufficiently large in some regions the resulting local stress concentration will produce yielding and plastic flow. This plastic deformation will result in agglomeration of large numbers of dislocations and may result in stacking faults. It is also possible that imperfect deposition causes excessive numbers of vacancies and dislocations. Any of these phenomena could provide an explanation for the diminution of the lattice parameter which accompanies the relief of strain.

It does not seem necessary to provide an elegant explanation of the anisotropy of the strain. Williamson and Smallman¹¹ have shown that carbon atoms in certain interstitial positions lead to anisotropic strain. While the strains they considered are about one-hundredth the size of those observed here, the same cause could produce the anisotropic strain found in the present work.

An obvious interpretation of the crystallite size anisotropy is that deposition occurs in such a way that platelets are formed, the major platelet plane being a given crystallite plane. However, since a great number of shapes can explain the observed anisotropy it is almost impossible to determine the correct one. Another possibility which was examined was that of stacking faults on the (211) planes. It was found that stacking faults alone could not explain the various crystallite sizes in this material. It has been shown by Warren and Warekois¹² that stacking faults in a cold-worked face-centered cubic material (a brass) are chiefly responsible for the apparent crystallite size. However, even with stacking faults every 20 planes, the results here would still require that the crystals be non-spherical, with a mean crystallite dimension of about 150 Å.

It was found (see Section 2.4.3) that the spacing of the (211) planes of the annealed powder was smaller than that of the untreated powder by 0.14 percent. Barrett¹³ has shown that stacking faults on (211)

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planes require a 58 percent increase in the spacing at the fault. To explain the observed difference in spacing on the basis of (211) stacking faults requires such faults about every 40 planes. However, the (110) spacing was found to differ by 0.27 percent. This is not what should be expected for (211) stacking faults and no explanation for this has yet been found.

A further corroboration that large strain is present in the untreated powder is given by Altmann¹⁴ who points out that untreated carbonyl iron is a very hard material (Vickers hardness 850), and softens considerably on annealing. The hardness is presumably due to a kind of strain hardening.

2.4.3 Annealing of the Experimental Carbonyl Fe Powder

Experimental Method - In order to learn something of the nature of the distortion, and of the causes of the apparent small crystallite size of this Fe carbonyl, powders were heat treated for two hours at 150°C, 250°C, 300°C, 350°C, 400°C and 450°C. The powders were then pressed into briquettes similar to those used in the work described in Section 2.4.2 of this report.

The details of the experimental method were changed in some respects from those described above, because of the greater number of lines that were involved in the analyses. The line profiles were obtained from these samples by automatic recording of the intensities from the Geiger tube on a strip chart recorder. The accuracy of lines obtained in this way is not as great as for "point by point" counting, but the agreement of results obtained on untreated powder by this method and by "point by point" counting was sufficiently good so that the difference in labor involved makes the automatic recording virtually mandatory.

In addition to the change in the method of recording intensities, only lines of the (110) set were analyzed in detail for

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the anneal study. For this work, FeK α was the only radiation used and consequently only the (110), (211), (220) lines were analyzed. The latter could be analyzed only for the higher temperature anneals where the intensity was appreciable. These, of course, represent different crystallographic planes rather than different orders of the same plane, but the data of Section 2.4.2 of this report indicate that this procedure is valid.

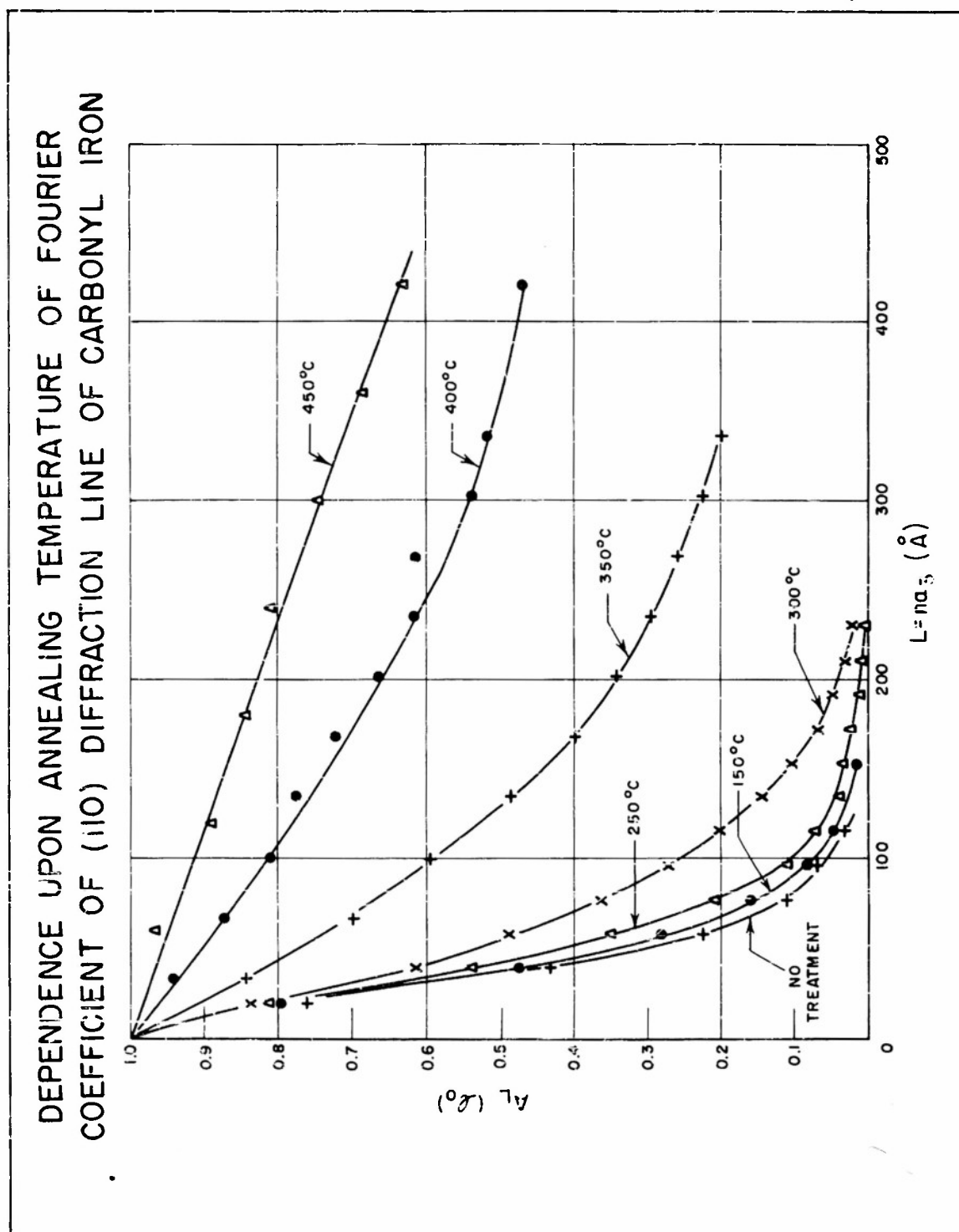
In all other respects the method of determining the crystallite size and strain was similar to that described in Section 2.4.2 of this report.

Results - In addition to the strain and crystallite size, the relative peak-heights, half-breadths, and the line positions of the (110) lines were determined as a function of temperature, and are tabulated in Table 2.2. These quantities were determined in order to obtain a qualitative picture of the annealing process.

Table 2.2 Diffraction Line Parameters as a Function of Annealing Temperature for Carbonyl Fe

Anneal Temp. (°C)	Peak Height Arbitrary Units	Half-breadths ($\Delta 2\theta$ - (deg.))	Line Positions (2θ - deg.)
No Treatment	18.5	1.165	58.88
150	19	1.150	56.90
250	21	1.000	56.92
300	29	0.700	56.95
350	62	0.320	57.01
400	92	0.240	57.01
450	108 (?)	0.225	57.03
Standard	255	0.130	57.04

A more or less "pictorial" view of the effects of annealing temperatures may be seen in Figure 2.6. where we have plotted A_L as a function of distance in the crystal, for various temperatures, for the



(110) line. In particular the large differences in the lines at 300°C and at 350°C show graphically the fact that the strain is reduced to 15% of its original value at 350°C, and also that this is the lowest annealing temperature studied for which there is an appreciable change in particle size.

Figure 2.7 is a combined plot of the strain and crystallite size in the (110) direction, and the peak position of the (110) line, as functions of annealing temperatures. The values shown in Figure 2.7 are summarized in Table 2.3.

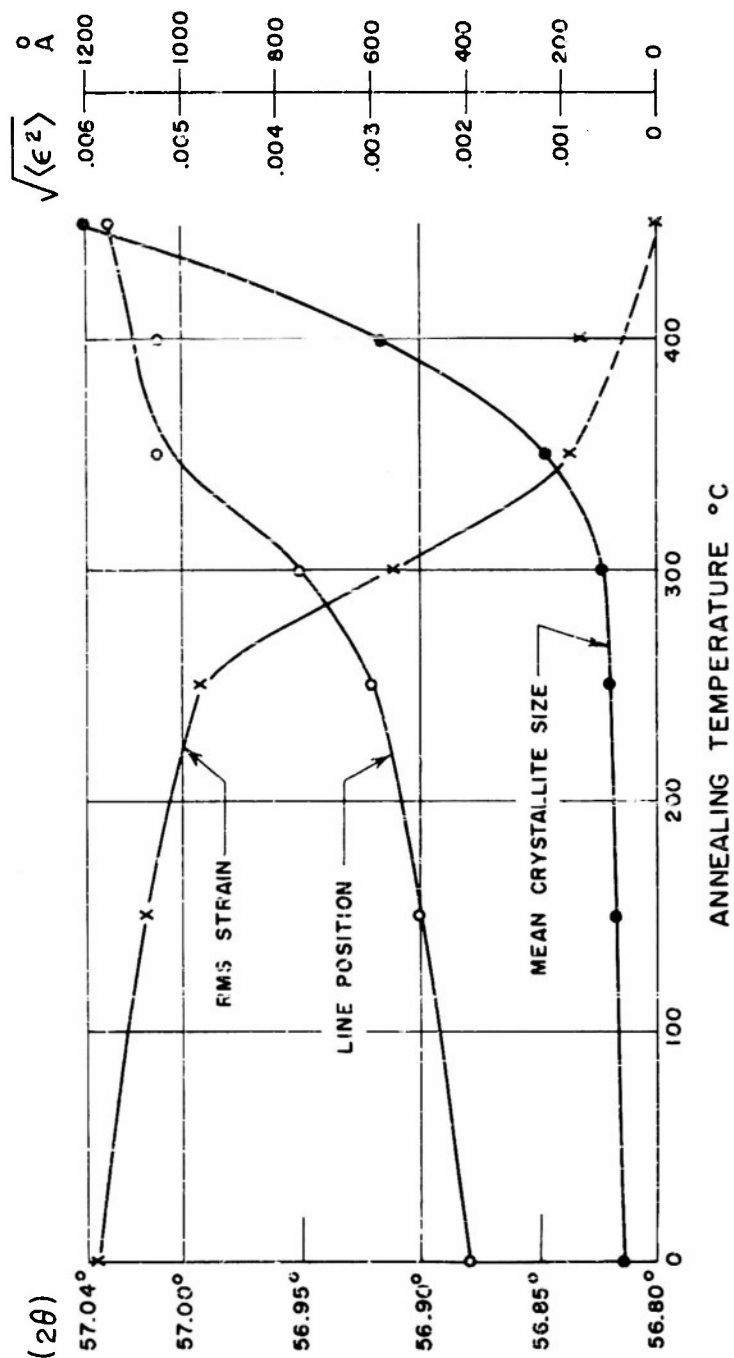
Table 2-3 Crystallite Size and Strain as a Function of Annealing Temperature for the [110] Direction

Anneal Temp. (°C)	Mean Crystallite Size (Å)	rms Strain	Line Position (110) Line (2θ in deg.)
No treatment	73	5.9×10^{-3}	56.88
150	84	5.4×10^{-3}	56.90
250	101	5.8×10^{-3}	56.92
300	116	2.8×10^{-3}	56.95
350	230	0.9×10^{-3}	57.01
400	580	0.8×10^{-3}	57.01
450	1200	---	57.03

Discussion of Results - Figure 2.7 shows that both line position and strain have almost reached their equilibrium value after 2 hrs. at 350°C.* It is evident that the major effect of the anneal at this temperature has been a strain recovery, since the crystallite size has only begun to increase. According to the manufacturer, sintering in

* Barrett¹⁵ discusses in some detail the recovery of line sharpness observed by other workers on materials in which such recovery occurred before recrystallization.

DEPENDENCE UPON ANNEALING TEMPERATURE OF MICROSCOPIC PROPERTIES OF CARBONYL IRON



these powders starts at 300°C. This indicates atomic mobility and is perhaps suggestive of the nature of the strain relief. Cottrell¹⁶ states that annealing causes migration and dissolution of dislocations and simultaneous motion of solute atoms to the region of high density of dislocations. It is then probable that these dislocations and impurity atoms form agglomerates at the boundaries of what may be called "subcrystals", the interior of which are now more perfect. It is the subcrystal size which is measured by X-rays, since the scattering from different subcrystals is presumed to be incoherent. With increasing annealing temperature, the subcrystal walls move and give a kind of grain growth, in situ. Since it is more difficult to move these walls than to move isolated defects to a boundary it is to be expected that strain recovery occurs at lower temperature than crystallite growth.

2.4.4 Conclusions

For this P-818 carbonyl iron, the following conclusions can be drawn:

- (1) The crystallites are non-spherical, and in all probability are platelets;
- (2) Recovery occurs at 350°C, presumably by a Cottrell mechanism;
- (3) The strain present is due to lattice defects which produce a lattice expansion. The most likely defects are impurity atoms, but vacancies or other dislocation defects have not been ruled out.
- (4) Crystallite growth occurs at temperatures below the generally-accepted recrystallization temperature (550°C), presumably by motion of subcrystal walls; and
- (5) Stacking faults on (211) planes alone are incapable of explaining the crystalline anisotropy.

3. FUTURE PLANS

With the completion of the study of the reduction process, attention will be devoted to the properties of alloy powders. For the FeBe_2 material, the powders will be formed initially by grinding melted material, and classifying into various sizes. At the same time, the reduction process will be used to prepare FePt powders. In both cases, studies of the effect of particle size on coercive force will be made, as well as measurements of the basic ferromagnetic properties.

The studies of the magnetic properties of powder compacts will be continued. Comparison between domain theory predictions and experimental results will be made concerning the effects of magnetic dilution on the shapes of the hysteresis loops, using the already-determined loops for the single-domain compacts discussed in this report. If possible, these results will be applied to mixtures of powders of different coercive forces, etc.

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Since this investigation is still in progress, the conclusions expressed in this report are tentative.

REFERENCES

- (1) L. Weil, *Compte Rendu* 225, 229 (1947)
- (2) A. R. Stokes, *Proc. Roy. Soc.* 61, 382 (1948)
- (3) H. Lipson and C. A. Beevers, *Proc. Phys. Soc.* 48, 772 (1936)
- (4) M. McKeehan and B. E. Warren, *J. Appl. Phys.* 24, 52 (1953)
- (5) B. E. Warren and B. L. Averbach, *J. Appl. Phys.* 21, 595 (1950)
- (6) B. E. Warren and B. L. Averbach, *J. Appl. Phys.* 23, 497 (1952)
- (7) B. E. Warren and B. L. Averbach, *J. Appl. Phys.* 23, 1059 (1952)
- (8) B. E. Warren and B. L. Averbach, Imperfections in Nearly Perfect Crystals, John Wiley and Sons, N. Y., 1952, p. 152
- (9) A. Taylor, Pittsburgh Diffraction Conference, Nov. 7, 1952
- (10) Felix Berteaut, Ph. D. Thesis, University of Grenoble, (1949)
- (11) G. K. Williamson and R. E. Smallman, *Acta. Cryst.*, 6, 361 (1953)
- (12) B. E. Warren and E. P. Warekois, *J. Appl. Phys.* 24, 951 (1953)
- (13) C. S. Barrett, *Progress in Metal Physics*, Vol. 3, Pergamon Press, London, 1952, p. 1
- (14) G. D. Altmann, *F. M. T. V.*, June 1949
- (15) C. S. Barrett, *Structure of Metals*, 2nd Ed., McGraw-Hill Co., N. Y., 1952, p. 435
- (16) A. H. Cottrell, *Progress in Metal Physics*, Vol. 1, Butterworths Scientific Publications, London, 1949, p. 77

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